



# Palladium–copper electrocatalyst for the promotion of the electrochemical oxidation of polyalcohol fuels in the alkaline direct alcohol fuel cell

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## ARTICLE INFO

### Article history:

Received 8 December 2014

Received in revised form 11 March 2015

Accepted 17 March 2015

Available online 19 March 2015

### Keywords:

Bi-functional effect

Electronic effect

Direct ethylene glycol fuel cell

Direct propylene glycol fuel cell

Direct glycerol fuel cell

## ABSTRACT

We demonstrate herein two important features of a Pd<sub>87</sub>Cu<sub>13</sub>/C electrocatalyst that indicate it is a more efficient catalyst in alkaline media than Pd/C for the electrochemical oxidation of three polyalcohols: ethylene glycol, propylene glycol, and glycerol. First, we have discovered more efficient behavior in a three electrode electrochemical cell, where the electrochemical oxidation rate of ethylene glycol and propylene glycol was 4 times faster on Pd<sub>87</sub>Cu<sub>13</sub>/C than Pd/C. In glycerol, the oxidation rate was 3 times faster in the electrochemical cell. This increase in oxidation rate is due to a combination of the electronic and bifunctional effects. Second, we have found that the Pd<sub>87</sub>Cu<sub>13</sub>/C catalyst is also more efficient than Pd/C in an operating alkaline direct liquid fuel cell, although the efficiency gains are smaller than the electrochemical cell. During fuel cell testing, we found that the maximum power density of a propylene glycol fuel cell was 86% greater when the anode catalyst was Pd–Cu/C compared with Pd/C. The maximum power densities of the glycerol and ethylene glycol fuel cells increased by 75% and 32%, respectively. These polyalcohol molecules are of significant interest because they can be made from renewable sources and used to produce power in alkaline direct liquid fuel cells.

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## 1. Introduction

Recent development of an alkaline anion exchange membrane (AEM) has sparked interest in the efficient utilization of small organic molecules as fuels for direct liquid fuel cells (DLFCs) [1–4]. The alkaline environment of such DLFCs is advantageous for three key reasons [5]. First, electrochemical oxidation of small organic molecules is more efficient in alkaline media since it occurs with lower overpotential. Second, there is no fuel crossover within the fuel cell because the ion transfers through the membrane from cathode to anode. Third, there is no concern with cathode water management since water is produced only at the anode.

The first studies of the AEM in a fuel cell were focused on ethanol due to its availability as a renewable fuel and its limitations in acidic media [6,7]. Since the development of the first alkaline direct ethanol fuel cell (DEFC), other fuels have been explored. Propanol and the polyalcohols ethylene glycol (EG), propylene glycol (PG), and glycerol (G), have all been used as fuels in alkaline DLFCs [8–16]. We recently demonstrated that all of these alcohol fuels can be used

in the same DLFC since they all oxidize on a palladium catalyst surface [17]. The most efficient fuel reported to date is potassium formate. The direct formate fuel cell (DFFC) has been demonstrated to produce more than twice the maximum power density (over 300 mW cm<sup>−2</sup>) of any of the alcohol fuels [18–22]. In addition, formate has been shown to be the only fuel that is capable of producing continuous power without addition of potassium hydroxide to the fuel stream, since its oxidation reaction rate is not dependent on the pH of the fuel stream [23].

While the polyalcohol fuels are the most energy dense of the aforementioned small organic molecules, they produce less power density in the DLFC than the other alcohols and the formate [17]. However, it is desirable to use these polyalcohols in the DLFC because they can be sourced renewably from cellulosic feedstock (EG and PG) and as a byproduct of biodiesel production (G) [24–28]. Hence, it is imperative that catalysts more efficient than Pd are developed for the electrochemical oxidation of polyalcohols in alkaline media; such catalysts should promote efficient use of these renewable, energy-dense fuels in liquid DLFCs.

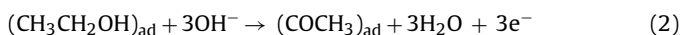
Recently, we demonstrated that the electrochemical oxidation of these polyalcohol fuels became significantly more efficient by the careful addition of small quantities of Sn, Sb, or Pb, at the palladium surface [29]. For example, the oxidation rate of G on Pd–Pb was 23

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times greater than on Pd after 10 min and 7.1 times greater after 12 h. In addition, the electrochemical oxidation of EG on Pd has also been shown recently to be promoted by the addition of Bi or Ni/Zn to the Pd [15,30]. Finally, we developed a Pd<sub>87</sub>Cu<sub>13</sub>/C catalyst that was shown to increase the electrochemical oxidation rate of ethanol and formate, but this catalyst has not previously been examined for polyalcohols [31].

The enhancement to electrochemical oxidation due to an element being added to Pd has been attributed to the bi-functional effect or the electronic effect (or a combination of both). The bi-functional effect occurs when the additional element directly catalyzes the electrochemical oxidation of the alcohol [5,15,32–34]. For example, the electrochemical oxidation of ethanol occurs on Pd by the following mechanism with the third reaction as the rate determining step [5,35]



Although the elements listed previously (Sn, Sb, Pb, Bi, Ni, Zn) are not known to directly adsorb ethanol, hydroxyls are more readily adsorbed on these non-noble metals than on the noble metal Pd [36]. Therefore, the bi-functional effect could result in a faster electrochemical oxidation rate for ethanol. It is also known that polyalcohol molecules require hydroxyl groups at the surface during oxidation, although their oxidation mechanisms are not as well understood [5].

The electronic effect occurs when the electronic structure of the Pd is modified by the presence of some other metal with a different d-orbital filling [37,38]. The resulting shift in Pd binding energy and d-band center changes the interaction of the Pd with the small organic molecule that is being oxidized [39,40]. When the changes to the Pd electronic structure are favorable, the reaction rate on the Pd is increased. It is difficult to distinguish between these two effects, although the reaction mechanisms offer some clues. For example, the electrochemical oxidation of formate occurs on a Pd surface by the following mechanism [21]:



which does not require the adsorption of a hydroxyl. Therefore, we did not expect the bi-functional effect to play a significant role in the electrochemical oxidation of formate, while it may play a significant role in the electrochemical oxidation of alcohols [31].

We previously reported physical and chemical characterization results on Pd/C and Pd<sub>87</sub>Cu<sub>13</sub>/C made by wet synthesis using sodium hypophosphite reducing agent and used in this work [31]. We found that the particle size was  $4.7 \pm 0.9$  nm for the Pd/C and  $5.0 \pm 1.2$  nm for the Pd–Cu/C. We identified a slight shift in the X-ray diffraction pattern indicating compression of the lattice due to alloying of Cu with Pd. Using these catalysts, we found an increase in the electrochemical oxidation rates of ethanol and formate in alkaline media. We attributed this to a combination of the electronic and bi-functional effects in ethanol and the electronic effect in formate. With respect to the electronic effect, we determined that there was an upshift in Pd 3d<sub>5/2</sub> binding energy for Pd–Cu/C compared with Pd/C; this was a result of Pd valence electrons moving toward Cu. Since electrochemical oxidation of ethanol requires adsorbed hydroxyl in the rate determining step (Eq. (3)), we expected that its oxidation would be more influenced by the bifunctional effect, whereby the presence of Cu makes hydroxyl adsorption more favorable [5,31,35,36].

In the present work, we compare the electrochemical oxidation rates of the three polyalcohols (EG, PG, and G) on Pd<sub>87</sub>Cu<sub>13</sub>/C to their oxidation rates on Pd/C in an electrochemical cell. We then expand on this work to demonstrate the behavior of this Pd–Cu/C catalyst in an operating alkaline DLFC using each of the 3 polyalcohols.

## 2. Experimental

### 2.1. Catalyst synthesis

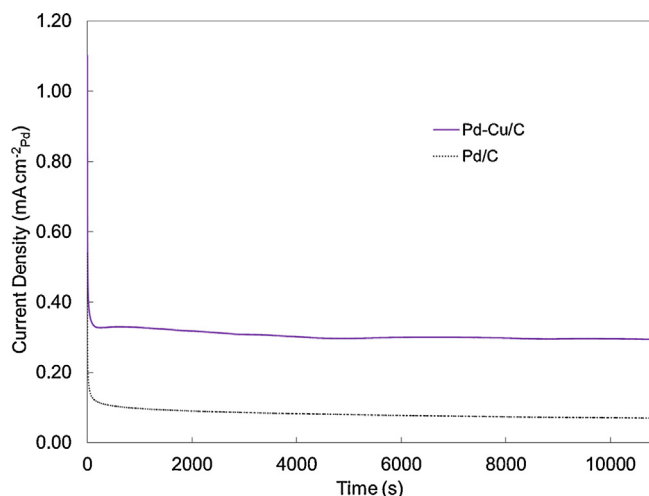
Each catalyst was prepared using metal salt reduction synthesis as described in our previous work [31]. In summary, sodium hypophosphite was used to reduce palladium and copper aqueous salts on activated Vulcan carbon. The solution was stirred, and sodium hydroxide and polyvinyl alcohol were added to control particle size. Proper atomic ratios of Pd and Cu precursors were used to produce Pd<sub>87</sub>Cu<sub>13</sub>/C and Pd/C. These catalysts were previously characterized using transmission electron microscopy, carbon analysis, elemental analysis, and X-ray diffraction [31].

### 2.2. Electrochemical analysis

Electrochemical measurements were performed using a PAR263A potentiostat in a custom-designed, three-electrode electrochemical cell. Catalyst ink was prepared using the carbon supported nanoparticles, AS-4 binder (Tokuyama, 15 wt% of final ink mass), and water. After sonication, a drop of this ink was dried onto a gold disk working electrode. The gold disk was rotated at 2000 rpm to remove gases produced during oxidation. The counter electrode was a platinum mesh (Alfa Aesar), and the reference electrode was a saturated calomel electrode (SCE, CH Instruments). Chronoamperometry was performed at  $-0.4$  V vs SCE in each of the polyalcohols (1 M polyalcohol + 1 M KOH) for 3 h, where the polyalcohol is either ethylene glycol, propylene glycol, or glycerol (Fisher). Cyclic voltammetry was also performed in 1 M glycerol + 1 M KOH at  $30 \text{ mVs}^{-1}$ . Cyclic voltammetry measurements of the catalysts were also performed using data from the first sweep in acid solution prior to oxidation of Cu (i.e., 1 M H<sub>2</sub>SO<sub>4</sub>) to estimate their electrochemically active surface areas [41]. Once a catalyst was examined in the acid solution, it was not used again in the polyalcohol due to leaching of copper from the nanoparticles.

### 2.3. Fuel cell analysis

Fuel cell measurements were performed using a DC load box (BK Precision, 8500), a custom-designed active fuel cell with a  $4 \text{ cm}^2$  electrode area, and the fuel cell heated to  $60^\circ\text{C}$ . The membrane electrode assembly (MEA) was an alkaline AEM (Tokuyama, A201) spray painted with  $2 \text{ mg cm}^{-2}$  Pd/C or Pd<sub>87</sub>Cu<sub>13</sub>/C total metal loading at the anode, platinum black (Alfa Aesar, high surface area) at the cathode, and carbon cloth diffusion layers (Fuel Cell Stores) at both electrodes. Prior to spray painting, the catalyst inks were prepared with 6 parts catalyst, water (cathode) or isopropanol (anode), and 1 part alkaline ionomer (Tokuyama, 5 wt% AS-4). During operation, the fuel stream was 1 M alcohol plus 2 M KOH at a flow rate of  $1 \text{ mL min}^{-1}$  for voltage current (VI) tests and  $0.2 \text{ mL min}^{-1}$  for constant current (CC) tests. The oxidant was pure, humidified oxygen at 100 sccm. During VI experiments, the voltage was stepped from open circuit to 0.1 V. The CC experiments were run at  $25 \text{ mA cm}^{-2}$ . Each fuel was run through the same membrane electrode assembly, since all fuels oxidize readily on the same Pd/Pt or Pd–Cu/Pt combination of anode/cathode catalysts [17].



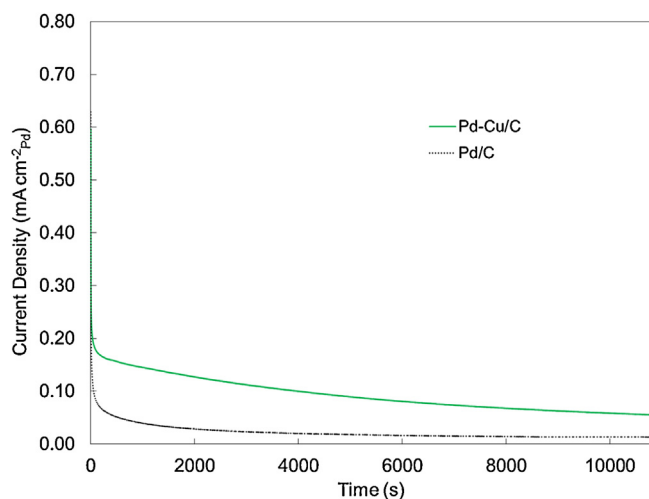
**Fig. 1.** Chronoamperometry of Pd–Cu/C and Pd/C at  $-0.4$  V vs SCE in 1 M KOH and 1 M EG. After 3 h, the oxidation rate on Pd–Cu/C is  $0.294 \text{ mA cm}^{-2}_{\text{Pd}}$ , while it is  $0.0699 \text{ mA cm}^{-2}_{\text{Pd}}$  on Pd/C.

### 3. Results and discussion

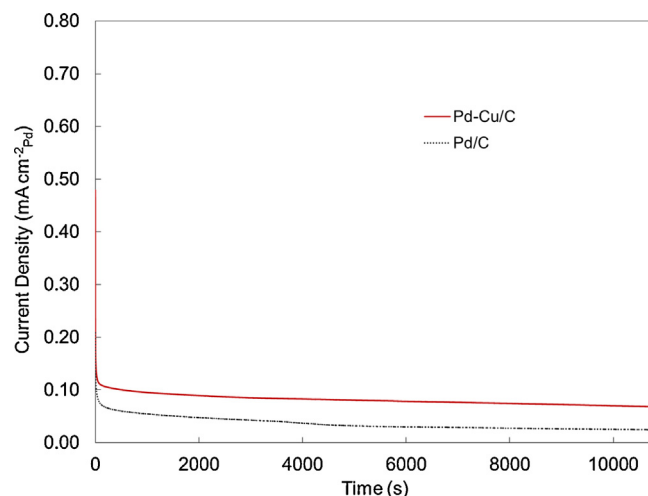
#### 3.1. Electrochemical comparison of Pd–Cu/C and Pd/C.

Recently, we discovered that heavy metals such as Sb, Sn, and Pb, greatly improved the electrochemical oxidation rate of polyalcohols when added to a Pd catalyst surface [29]. Therefore, the objective of the present work was to determine if Cu would also improve the electrochemical oxidation rate of polyalcohols when alloyed with carbon supported Pd. To test this hypothesis we first performed electrochemical characterization using chronoamperometry. Fig. 1 shows that the electrochemical oxidation rate of EG on Pd–Cu/C was  $0.294 \text{ mA cm}^{-2}_{\text{Pd}}$  after 3 h, which was more than 4 times greater than the oxidation rate of EG on Pd/C, which was only  $0.0699 \text{ mA cm}^{-2}_{\text{Pd}}$ . This 4-fold improvement to the oxidation rate was relatively stable during the entire 3 hours of oxidation.

A 4-fold increase in the electrochemical oxidation rate of PG was observed on Pd–Cu/C ( $0.0558 \text{ mA cm}^{-2}_{\text{Pd}}$ ) when compared to Pd/C ( $0.0134 \text{ mA cm}^{-2}_{\text{Pd}}$ ) after 3 h (Fig. 2). Finally, Fig. 3 shows that the rate of electrochemical oxidation of G increased 3-fold after 3 hours on Pd–Cu/C ( $0.0683 \text{ mA cm}^{-2}_{\text{Pd}}$ ) compared with Pd/C



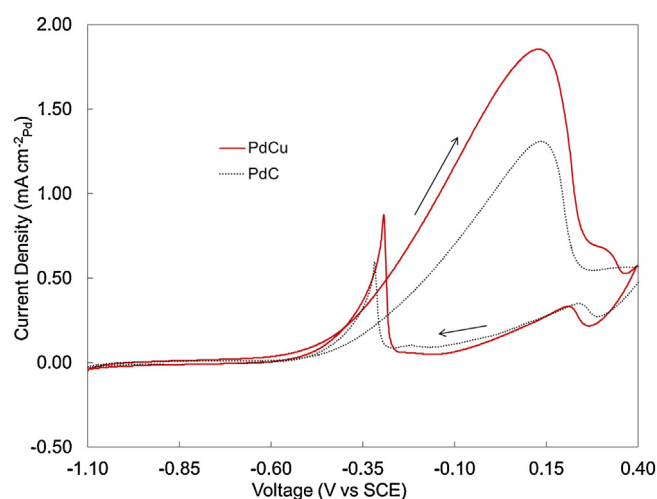
**Fig. 2.** Chronoamperometry of Pd–Cu/C and Pd/C at  $-0.4$  V vs SCE in 1 M KOH and 1 M PG. After 3 h, the oxidation rate on Pd–Cu/C is  $0.0558 \text{ mA cm}^{-2}_{\text{Pd}}$ , while it is  $0.0134 \text{ mA cm}^{-2}_{\text{Pd}}$  on Pd/C.



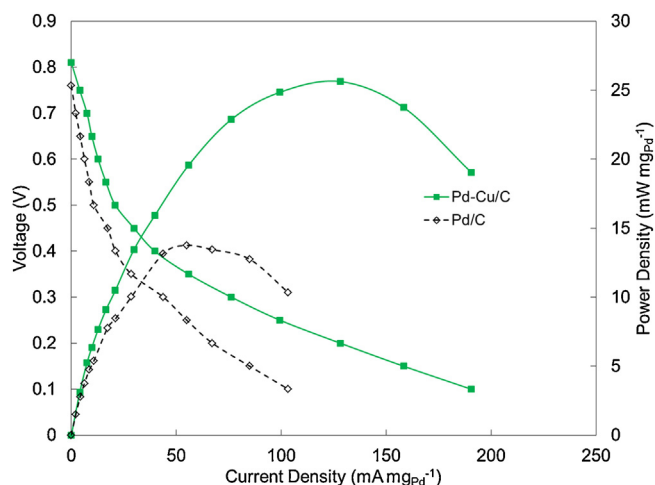
**Fig. 3.** Chronoamperometry of Pd–Cu/C and Pd/C at  $-0.4$  V vs SCE in 1 M KOH and 1 M G. After 3 h, the oxidation rate on Pd–Cu/C is  $0.0683 \text{ mA cm}^{-2}_{\text{Pd}}$ , while it is  $0.0245 \text{ mA cm}^{-2}_{\text{Pd}}$  on Pd/C.

( $0.0245 \text{ mA cm}^{-2}_{\text{Pd}}$ ). These results indicate that there is a stable, significant increase to the electrochemical oxidation rate of these three polyalcohols on Pd<sub>87</sub>Cu<sub>13</sub>/C as compared to the rate on Pd/C. The increase in oxidation rate on ethanol and formate was only 1.5 times and 1.2 times greater, respectively, after 30 min on the Pd–Cu/C compared to the Pd/C [31]. It has been proposed that polyalcohols require surface adsorbed hydroxyl molecules both for alcohol adsorption and desorption steps; therefore, one would expect the oxidation rate of polyalcohols to be more influenced by the presence at the surface of a non-noble metal such as Cu that can promote surface adsorption of hydroxyls [5,15,29]. Hence, it is likely that the bifunctional effect is playing a significant kinetic role in the electrochemical oxidation of EG, PG, and G, on Pd–Cu/C.

Cyclic voltammetry was also performed in the same solutions as the chronoamperometry to observe the behavior of the catalyst for electrochemical oxidation at different potentials. The voltammogram shown in Fig. 4 (in G) is the expected behavior for these alcohols since Pd does not easily break the C–C bond, which would lead to significant quantities of adsorbed C<sub>1</sub> intermediates that would be evident from the voltammogram; therefore, the behavior closely matches that of formate and ethanol where such evidence



**Fig. 4.** Cyclic voltammetry (cycle 3) of Pd–Cu/C and Pd/C in 1 M KOH and 1 M G at a sweep rate of  $30 \text{ mV s}^{-1}$ . The peak current density at  $0.1 \text{ V}$  is  $1.85 \text{ mA cm}^{-2}_{\text{Pd}}$  on the Pd–Cu/C, while it is  $1.31 \text{ mA cm}^{-2}_{\text{Pd}}$  on Pd/C.



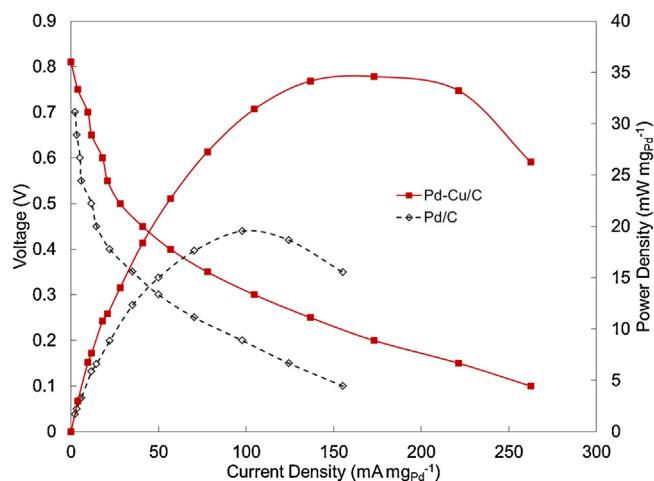
**Fig. 5.** Voltage–current (VI) plots in the direct PG fuel cell. Anode fuel was 1 M PG and 2 M KOH flowing at  $1 \text{ mL min}^{-1}$ . Anode catalysts were Pd–Cu/C or Pd/C. Cathode oxidant was humidified oxygen flowing at 100 sccm, and cathode catalyst was Pt black. Fuel cell temperature was 60 °C.

is not observed [5,31]. The current increases in the positive sweep until the surface Pd is deactivated ( $\sim 0.15 \text{ V}$ ) by oxide formation and reactivated after the surface oxides have been reduced from the Pd ( $\sim 0.30 \text{ V}$ ). The potential chosen for chronoamperometry ( $-0.4 \text{ V}$ ) is low so as to 1) avoid oxide deactivation of the Pd surface and 2) mimic the approximate potential of the anode during fuel cell operation (i.e., much lower than the peak oxidation potential). It is evident from Fig. 4 that the presence of the Cu in the Pd nanoparticles increases the current at all potentials following the onset of oxidation as expected, indicating a kinetic advantage to the presence of Cu in the Pd nanoparticles.

### 3.2. Fuel cell operation with polyalcohol fuels

While the electrochemical behavior of the Pd–Cu/C catalyst is of fundamental interest, its practical application is observed in its behavior in an operating alkaline direct liquid fuel cell. As we previously demonstrated, Pd catalyst is efficient for the oxidation of all three polyalcohols in this study, and the same membrane electrode assembly (MEA) can be used to oxidize all three fuels [17]. Therefore, in this work we used an MEA with Pd<sub>87</sub>Cu<sub>13</sub>/C painted at the anode to study the fuel cell behavior of the Pd–Cu/C catalyst, and we painted a second MEA with Pd/C at the anode for comparison. We found that the Pd–Cu/C catalyst promoted the fuel cell performance with each fuel. We observed the most significant promotion when using PG as fuel. As shown in Fig. 5, the maximum power density of the PG fuel cell with Pd–Cu/C anode catalyst was  $26 \text{ mW mgPd}^{-1}$ , which was 86% greater than the fuel cell with Pd/C anode catalyst ( $14 \text{ mW mgPd}^{-1}$ ). Fig. 6 shows that the maximum power density of the G fuel cell operated with Pd–Cu/C anode catalyst ( $35 \text{ mW mgPd}^{-1}$ ) was 75% greater than when operated with Pd/C anode catalyst ( $20 \text{ mW mgPd}^{-1}$ ). EG, which was already the most easily oxidized fuel (highest oxidation rate) in electrochemical tests on Pd/C, was promoted the least by Pd–Cu/C anode catalyst in the fuel cell (Fig. 7): the maximum power density only increased from 22 to  $29 \text{ mW mgPd}^{-1}$ , an increase of 32%. It is likely that EG benefited the least from the addition of Cu to the anode catalyst because it was already more efficient on Pd than the other catalysts during fuel cell operation.

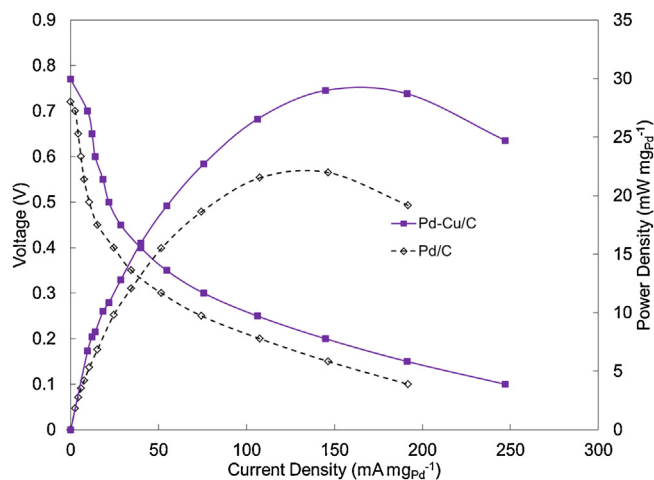
In comparing Fig. 5 through Fig. 7, it is important to note the contributions of three key losses in the fuel cells as represented in the VI plots. First, kinetic losses come from overpotentials and are observed in the high voltage, low current regions of the plot,



**Fig. 6.** Voltage–current (VI) plots in the direct G fuel cell. Anode fuel was 1 M G and 2 M KOH flowing at  $1 \text{ mL min}^{-1}$ . Anode catalysts were Pd–Cu/C or Pd/C. Cathode materials and fuel cell temperature were the same as Fig. 5.

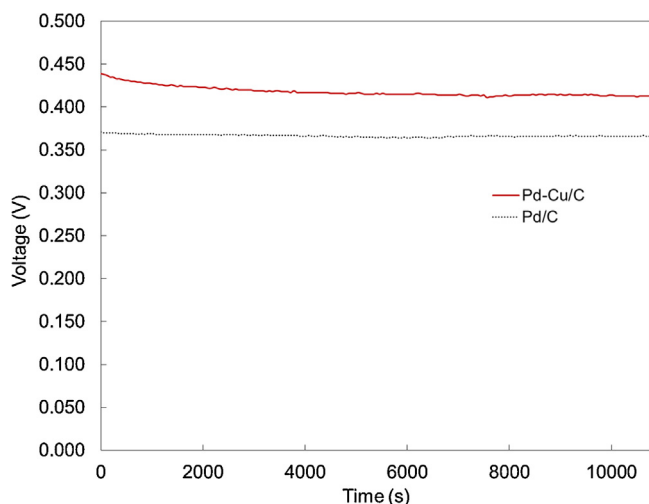
approximately,  $0\text{--}20 \text{ mA mgPd}^{-1}$  in these fuel cells (kinetic region). Second, ohmic resistance results in a loss of voltage as more current flows through the fuel cell as the current density is increased; this is observed in the negative and reasonably stable slope from low to high current density (ohmic region). Third, mass transport losses occur beyond the ohmic region at low voltage and high current density. In the VI plots, no mass transport region is observed above  $0.1 \text{ V}$ , but it likely exists below  $0.1 \text{ V}$ . Since the fuel cell is being operated with the same membrane and fuel cell assembly, no significant difference in the ohmic or mass transport regions of the VI plots is observed since the only significant change is to the anode catalyst. However, the most important difference is observed in the kinetic region, where the open circuit voltage is higher and the kinetic losses (drop in voltage with increase in current) are lower for each fuel when the anode catalyst is Pd<sub>87</sub>Cu<sub>13</sub>/C compared with when the anode catalyst is Pd/C. This indicates that the Pd–Cu/C catalyst improves the kinetic rate of the electrochemical oxidation of the polyalcohol fuels. Therefore, the kinetic improvement observed in the electrochemical cell is transferred to the fuel cell.

While the efficiency of the anode catalyst is known to be the limiting factor for alkaline direct liquid fuel cells, improvement of the anode alone provides somewhat less improvement to fuel cell



**Fig. 7.** Voltage–current (VI) plots in the direct EG fuel cell. Anode fuel was 1 M EG and 2 M KOH flowing at  $1 \text{ mL min}^{-1}$ . Anode catalysts were Pd–Cu/C or Pd/C. Cathode materials and fuel cell temperature were the same as Fig. 5.





**Fig. 8.** A constant current experiment at  $25 \text{ mA cm}^{-2}$  in the direct G fuel cell. Anode fuel was 1 M G and 2 M KOH flowing at  $0.2 \text{ mL min}^{-1}$ . Anode catalysts were Pd–Cu/C or Pd/C. Cathode materials and fuel cell temperature were the same as Fig. 5.

efficiency than what was observed in electrochemical measurements; this is not surprising due to the complex balance of plant of the operating fuel cell [5,42,43]. Regardless, the improvements we observe in fuel cell efficiency are significant. In order to confirm that the promotion by Cu was stable, we ran the fuel cell at a constant current of  $25 \text{ mA cm}^{-2}$  for 3 hours using G as the fuel (Fig. 8). We observed that the voltage at this current was higher on Pd–Cu/C and stable. These results in the operating fuel cell demonstrate that Pd–Cu/C is a more efficient catalyst than Pd/C for the electrochemical oxidation of EG, PG, and G, due to contributions from the bifunctional and electronic effect, with the most significant contributions likely coming from the bifunctional effects. The observation that the electrochemical behavior carries over to the fuel cell is important for the application of these catalysts, particularly for the oxidation of these polyalcohol fuels that can be derived from renewable sources.

#### 4. Conclusion

Our results demonstrate that  $\text{Pd}_{87}\text{Cu}_{13}/\text{C}$  is a more efficient catalyst (compared with Pd/C) for the electrochemical oxidation of polyalcohols (EG, PG, and G) in alkaline media. This same catalyst was previously shown to slightly promote the electrochemical oxidation rates of formate and ethanol by 1.2 and 1.5 times, respectively. The promotion was due to the electronic effect for formate and a likely combination of electronic and bi-functional effects for ethanol. Since polyalcohol molecules are more promoted by the bi-functional effect, we observed a more significant promotion of their oxidation rates: 4 times for ethylene glycol and propylene glycol and 3 times for glycerol. This promotion carried over to the fuel cell but was less pronounced as expected. The power density of the PG fuel cell was 86% greater when Pd–Cu/C was used at the anode compared to Pd/C. The EG maximum power density was 75% greater, and the G power density was 32% greater. These polyalcohol fuels are important because they can be made from renewable sources. We have shown that their oxidation rates, though sluggish compared to monoalcohols such as ethanol, can be significantly improved by the addition of Cu to the Pd catalyst.

#### Acknowledgements

Funding was provided by the Petroleum Research Fund (PRF# 53133-UNI5) and grant funds from California State University, Fullerton.

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